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(54) Title: BENZIMIDAZOLYL QUINOLINE-3-CARBOXYLATE DERIVATIVES, INTERMEDIATES THERETO, AND THEIR USE AS HERBICIDES				
(57) Abstract				
The invention relates to benzimidazolyl quinoline-3-carboxylate derivatives of formula (I), in which the various symbols are as defined in the description, and their use as herbicides.				

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BENZIMIDAZOLYL QUINOLINE -3- CARBOXYLATE DERIVATIVES, INTERMEDIATES THERETO, AND THEIR USE AS HERBICIDES

Technical Field

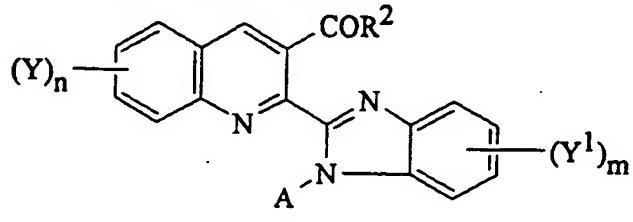
This invention relates to novel compounds, processes for their preparation, compositions containing them, intermediates in their synthesis and their use as herbicides.

Background Art

European Patent Application number 90420452.6 describes certain 2-azoyl nicotinate derivatives having herbicidal activity.

Disclosure of Invention

The present invention provides benzimidazolyl quinoline-3-carboxylate derivatives of formula I :-



(I)

wherein Y represents a straight- or branched- chain alkyl group containing up to eight carbon atoms which is optionally substituted by one or more R¹ groups which may be the same or different; or a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or a group selected from -SR, -S(O)R, -SO₂R, -OR, halogen, nitro, cyano, -NR⁷R⁸, aryl and O-aryl;

Y¹ represents a straight- or branched- chain alkyl, alkenyl or alkynyl group containing up to eight carbon atoms which is optionally substituted by one or more R¹ groups which may be the same or different; or a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or a group selected from -SR, -OR, -OR^{1a}, halogen, aryl, aralkyl, O-aryl, -NR⁷R⁸ or -OCH₂R¹¹;

R² represents a group -OH -NR⁷R⁸ or -X-M, where X represents oxygen or sulphur and

M represents a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or a cycloalkyl group containing from three to six carbon atoms optionally

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- substituted by one or more R¹ groups which may be the same or different; or a group selected from aryl, aralkyl, -(CR⁴¹R⁴²)_q-C≡CR⁶, -(CR⁴¹R⁴²)_q-C(R⁴)=CR⁵R⁶ and -N=CR⁹R¹⁰;
- 5 A represents -SO₂NR⁷R⁸;
R represents a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more groups R¹ which may be the same or different; or a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more groups R³ which may be the same or different;
- 10 R¹ represents a group selected from -OR³, -S(O)_sR³, wherein s is zero, one or two, halogen, a cycloalkyl group containing from 3 to 6 carbon atoms (optionally substituted by one or more groups R¹ which may be the same or different, other than cycloalkyl), R³,
- 15 O-aryl, cyano or -CO₂R⁵;
R^{1a} is -(CR⁴R⁵)₁-C≡CR⁶ or -(CR⁴¹R⁴²)₁-C(R⁴)=CR⁵R⁶;
R³ represents a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more halogen atoms which may be the same or different;
- 20 R⁴, R⁴¹, R⁴² and R⁵, which may be the same or different, each represent hydrogen or a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more halogen atoms which may be the same or different; or aryl;
- 25 R⁶ represents a group selected from R⁴ or aralkyl;
R⁷ and R⁸, which may be the same or different, each represent a hydrogen atom a group selected from R, -OR³, -S(O)_sR³, halogen, R³, O-aryl, aryl or aralkyl; or R⁷ and R⁸ may form together with the nitrogen to which they are attached a heterocycle containing from 3 to 6 carbon atoms in the ring and zero, 1 or 2 additional heteroatoms in the ring selected from nitrogen, oxygen and sulphur;
- 30 R⁹ and R¹⁰, which may be the same or different, each represent:
a hydrogen atom or a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more groups, which may be the same or different, selected from halogen, -OR or -S(O)_sR, where s is zero, 1 or 2; or phenyl optionally substituted by from one to four groups, which may be the
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- same or different, selected from nitro, R, -NR⁴R⁵, halogen or -S(O)₅R; or a 5 or 6 membered heterocycle containing from 3 to 5 carbon atoms in the ring and one or more heteroatoms in the ring selected from nitrogen, sulphur or oxygen, e.g. thienyl, furyl,
5 piperidyl, thiazolyl, optionally substituted by one or more groups R¹ which may be the same or different;
or R⁹ and R¹⁰ may form together with the nitrogen to which they are attached a heterocycle containing 4 or 5 carbon atoms in the ring, which may be optionally substituted by from 1 to 3 groups
10 R³ which may be the same or different;
R¹¹ represents a five or six membered aliphatic ring comprising an oxygen atom in the ring;
'aryl' represents a phenyl group optionally substituted by from one to four groups which may be the same or different selected
15 from -OR³, -SR³, halogen or R³; or a 5 or 6 membered heterocycle containing from 3 to 5 carbon atoms in the ring and one or more heteroatoms in the ring selected from nitrogen, sulphur or oxygen, e.g. thienyl, furyl, piperidyl, thiazolyl; optionally substituted by one or more groups, which may be the same or different, selected from -
20 OR³, -SR³, halogen or R³;
aralkyl represents a group-(CR⁴R⁵)_p-aryl (e.g. benzyl);
m represents zero or an integer from 1 to 4, the groups Y¹ being the same or different when m is greater than 1; n represents an integer from 1 to 4; p represents one or two; q represents one
25 or two; r represents an integer from 1 to 5;
where p, q or r is greater than 1, the groups -(CR⁴R⁵)- and the groups -(CR⁴¹R⁴²)- may be the same or different;
where n is greater than 1 no more than one of the groups Y represents nitro, -SR, -SOR, -SO₂R, nitro, -NR⁷R⁸, aryl or O-aryl;
30 and agriculturally acceptable salts thereof, which possess valuable herbicidal properties.
Furthermore, in certain cases the substituents Y, Y¹, R² and A may give rise to optical isomerism and/or stereoisomerism. All such forms are embraced by the present invention.
35 By the term "agriculturally acceptable salts" is meant salts the cations or anions of which are known and accepted in the art for the formation of salts for agricultural or horticultural use. Preferably the salts are water-soluble.

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It is to be understood that where reference is made in the present specification to the compounds of formula I, such reference is intended to include salts where the context so permits.

5 A particularly important class of compounds because of their herbicidal properties are those in which:

(a) R represents a group $\text{-SO}_2\text{NR}^7\text{R}^8$ in which R⁷ and R⁸ each represents an alkyl group, preferably methyl;

10 (b) R² represents a group -OH, -XM or -XW in which X is preferably oxygen, M is preferably alkynyl, eg propargyl, and W is an agriculturally acceptable cation, eg Na, K, Li or an ammonium cation such as isopropylammonium;

15 (c) Y represents alkyl, eg methyl or ethyl; alkoxy, eg methoxy; a halogen, eg chlorine or fluorine; and n is 1 or 2; compounds in which n is 1 and the substituent Y is in the 6- position of the quinoline ring are preferred;

20 (d) Y¹ represents a group OR or SR, eg methoxy, ethoxy, i-propoxy, n-propoxy, trifluoromethoxy, difluoromethoxy or cycloalkylmethoxy or cycloalkylmethylthio, eg cyclopropylmethoxy or cyclopropylmethylthio; halogen, eg chlorine or fluorine; alkyl, eg methyl; a group -OR^{1a} or -SR^{1a}, eg allyloxy or propargyloxy; and m is 0, 1 or 2; compounds in which m is 1 and the substituent is in the 4 or 5 position of the benzimidazole ring are preferred, as are compounds in which m is 2 and the substituents, which may be the same or different, are in the 4- and 5- positions of the benzimidazole ring. Compounds of formula I in which Y represents methyl, ethyl or chlorine are particularly preferred. Preferably the quinoline ring is substituted in the 6- position by a group Y.

25 Preferably the benzimidazole ring is substituted in the 4- and/or 5- position by a group Y¹. Where the benzimidazole ring is substituted in the 4- position Y¹ is preferably a group selected from methyl, methoxy, ethoxy, n-propoxy, allyloxy, propargyloxy, 2-methoxyethoxy and chlorine. Where the benzimidazole ring is substituted in the 5- position Y¹ is preferably a group selected from methyl, chlorine and fluorine.

30 35 Compounds in which n is one are especially preferred.

Particularly important compounds include the following:-

1. 2-(1-N,N-Dimethylsulphamoylbenzimidazol-2-yl)-6-ethylquinoline-3-carboxylic acid.
2. 2-(1-N,N-

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- Dimethylsulphamoylbenzimidazol-2-yl)-6-methoxyquinoline-3-carboxylic acid. 3. 2-(1-N,N-Dimethylsulphamoylbenzimidazol-2-yl)-6-methylquinoline-3-carboxylic acid. 4. 2-(1-N,N-Dimethylsulphamoylbenzimidazol-2-yl)-8-methylquinoline-3-carboxylic acid. 5. 2-(1-N,N-Dimethylsulphamoylbenzimidazol-2-yl)-5,8-dimethylquinoline-3-carboxylic acid. 6. 2-Propynyl 2-(1-N,N-dimethylsulphamoylbenzimidazol-2-yl)-6-ethylquinoline-3-carboxylate. 7. 2-Propynyl 2-(1-N,N-dimethylsulphamoylbenzimidazol-2-yl)-6-methoxyquinoline-3-carboxylate. 8. Methyl 2-(1-N,N-dimethylsulphamoylbenzimidazol-2-yl)-6-methylquinoline-3-carboxylate. 9. 2-Propynyl 2-(1-N,N-dimethylsulphamoylbenzimidazol-2-yl)-8-methylquinoline-3-carboxylate. 10. 2-Propynyl 2-(1-N,N-dimethylsulphamoylbenzimidazol-2-yl)-5,8-dimethylquinoline-3-carboxylate. 11. 2-[(1-N,N-Dimethylsulphamoyl)-4-(2-propynyoxy)-benzimidazol-2-yl]-6-methylquinoline-3-carboxylic acid. 12. 2-[(1-N,N-Dimethylsulphamoyl)-4-methoxybenzimidazol-2-yl]-6-methylyquinoline-3-carboxylic acid. 13. 2-[(1-N,N-Dimethylsulphamoyl)-4-(2-propenoxy)-benzimidazol-2-yl]-6-methylquinoline-3-carboxylic acid. 14. 2-[(1-N,N-Dimethylsulphamoyl)-4-difluoromethoxy-benzimidazol-2-yl]-6-methylquinoline-3-carboxylic acid. 15. 2-[(1-N,N-Dimethylsulphamoyl)-4-ethoxybenzimidazol-2-yl]-6-methylquinoline-3-carboxylic acid. 16. 2-[(1-N,N-Dimethylsulphamoyl)-4-methoxybenzimidazol-2-yl]-6-ethylquinoline-3-carboxylic acid. 17. 2-[(1-N,N-Dimethylsulphamoyl)benzimidazol-2-yl]-6-chloroquinoline-3-carboxylic acid. 18. 2-[(1-N,N-Dimethylsulphamoyl)-4-methoxybenzimidazol-2-yl]-6-chloroquinoline-3-carboxylic acid. 19. 2-[(1-N,N-Dimethylsulphamoyl)-4-(2-propynyoxy)-benzimidazol-2-yl]-6-chloroquinoline-3-carboxylic acid. 20. Methyl 2-[(1-N,N-dimethylsulphamoyl)-4-(2-propynyoxy)-benzimidazol-2-yl]-6-methylquinoline-3-carboxylate. 21. Methyl 2-[(1-N,N-dimethylsulphamoyl)-4-methoxy-benzimidazol-2-yl]-6-methylquinoline-3-carboxylate. 22. Methyl 2-[(1-N,N-dimethylsulphamoyl)-4-(2-propenoxy)-benzimidazol-2-yl]-6-

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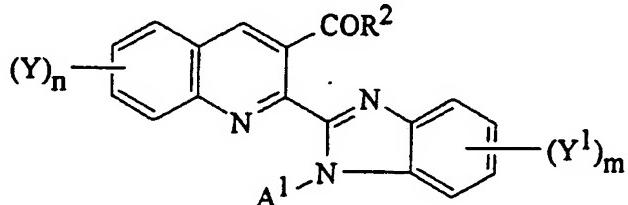
methylquinoline-3-carboxylate. 23. Methyl 2-[(1-N,N-dimethylsulphamoyl)-4-difluoromethoxy-benzimidazol-2-yl]-6-methylquinoline-3-carboxylate. 24. Methyl 2-[(1-N,N-dimethylsulphamoyl)-4-ethoxybenzimidazol-2-yl]-6-methylquinoline-3-carboxylate. 25. Methyl 2-[(1-N,N-dimethylsulphamoyl)-4-methoxybenzimidazol-2-yl]-6-ethylquinoline-3-carboxylate. 26. Methyl 2-[(1-N,N-dimethylsulphamoyl)benzimidazol-2-yl]-6-chloroquinoline-3-carboxylate. 27. Methyl 2-[(1-N,N-dimethylsulphamoyl)-4-methoxybenzimidazol-2-yl]-6-chloroquinoline-3-carboxylate. 28. Methyl 2-[(1-N,N-dimethylsulphamoyl)-4-(2-propynloxy)benzimidazol-2-yl]-6-chloroquinoline-3-carboxylate.

The numbers 1 to 28 are assigned to these compounds for reference and identification hereafter.

Processes for Carrying Out the Invention

The compounds of formula I can be prepared by the application or adaptation of known methods (i.e. methods heretofore used or described in the chemical literature), for example as hereinafter described.

According to a feature of the present invention compounds of formula (I) in which R² is a -XM or -NR⁷R⁸ radical can be prepared by reacting a sulphonamoyl chloride of the formula Cl-SO₂NR⁷R⁸ with a compound of formula (Ia):



(Ia)

in which A¹ is the hydrogen atom and R² is an -XM or -NR⁷R⁸ radical, in the presence of an acid acceptor such as potassium carbonate, triethylamine, 1,8-diazabicyclo[5.9.0]undec-7-ene or sodium hydride, preferably in an anhydrous medium using an aprotic polar solvent, for example, ethers (such as tetrahydrofuran) or nitriles, at a temperature which is generally between 25 °C and the reflux temperature of the solvent.

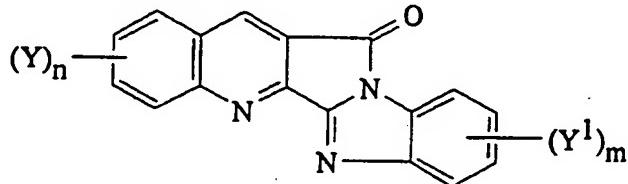
According to a further feature of the present invention compounds of formula (I) where R^2 is $-XW$ in which X represents

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oxygen may be prepared from compounds of formula (I) where R² is -OH by reaction with the corresponding base.

According to a further feature of the present invention
5 compounds of the formula (I) in which R² represents -OH, may be prepared by the hydrolysis of compounds of formula (I) in which R² represents the group -XM using an inorganic base, for example lithium hydroxide, in a mixture of water and an alcohol, for example methanol, at a temperature between 0 °C and 25 °C.

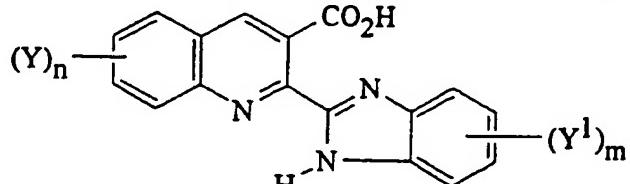
10 Intermediates in the preparation of compounds of formula I are prepared by the application or adaptation of known methods. Compounds of formula (Ia) in which A¹ is the hydrogen atom and R² is a radical -XM or -NR⁷R⁸ may be prepared by reacting a compound of formula (II) :



15 (II)

with an alkali metal alcoholate or alkaline earth metal
20 alcoholate of the formula XM-M', wherein M' represents an alkali metal or alkaline earth metal cation, in an aprotic solvent and at a temperature between 0°C and the boiling point of the solvent, or with an alcohol, thiol or oxime of the formula H-XM, or with an amine of the formula HNR⁷R⁸. The reaction with H-XM or HNR⁷R⁸ is generally performed in a polar organic solvent in the presence of an acid acceptor such as pyridine or triethylamine.

25 Compounds of formula (Ia) in which A¹ represents the hydrogen atom and R² is a radical -XM or -NR⁷R⁸ may be prepared by the reaction of the compound of formula (III) :



(III)

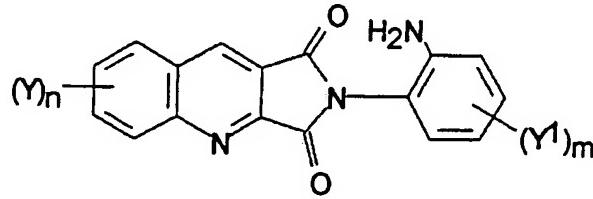
30 with an alcohol, thiol or oxime of formula H-XM or an amine of formula H-NR⁷R⁸ in the presence of a coupling reagent, for example N,N-dicyclohexylcarbodiimide, in the presence of an inert

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solvent such as dichloromethane and at a temperature between 0 °C and the reflux temperature of the solvent.

Compounds of formula (Ia) in which A¹ is the hydrogen atom and R² is a radical -XM in which X is the oxygen atom and M is as hereinbefore defined excluding the group -N=CR⁹R¹⁰, may be prepared by reacting a compound of formula (III) with a compound of formula H-OM in the presence of gaseous HCl with the compound of formula H-OM also acting as a solvent following a well known esterification process.

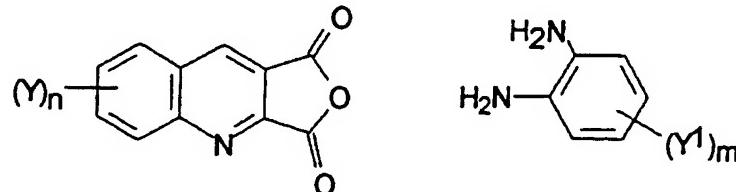
Compounds of the formula (Ia), where A¹ is the hydrogen atom and R² is the radical -XM, where X represents the oxygen atom and M is as hereinbefore defined excluding the group -N=CR⁹R¹⁰, may be prepared by heating a compound of formula (IIIa):



(IIIa)

in a high boiling compound of formula H-OM, where M has the abovementioned meaning, for example ethoxyethanol at temperatures between 50 °C and the reflux temperature of the solvent.

Compounds of formula (II') may be prepared by reacting a quinoline-2,3 dicarboxylic acid anhydride of formula (IV) with a 1,2-phenylenediamine of formula (V):



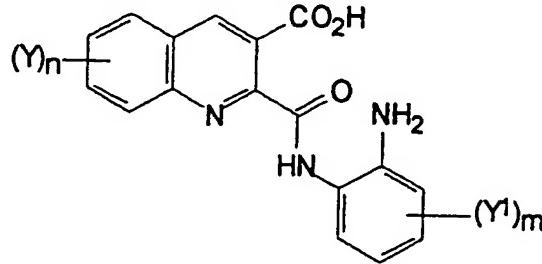
(IV)

(V)

by heating at temperatures between 110 and 190 °C for between 1 and 3 hours, either in the absence of a solvent or in a solvent such as xylene, dichlorobenzene, or acetic acid followed by the addition of acetic anhydride and continued heating at a temperature between 70 °C and the boiling point of the solvent.

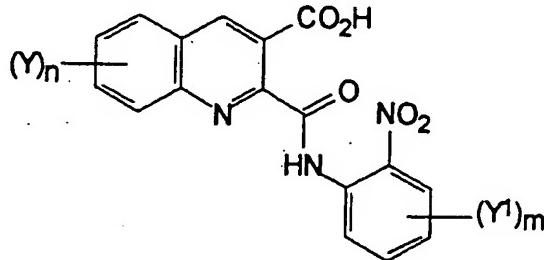
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Compounds of formula (III) may be prepared by the cyclisation of a compound of formula (VI) :



(VI).

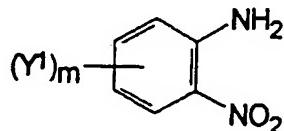
5 The reaction may be carried out in an organic solvent such as ethoxyethanol under reflux. Compounds of formula (VI) may be obtained by the reaction of a quinoline -2,3-dicarboxylic acid anhydride of formula (IV) with a 1,2-phenylenediamine of formula (V) in an inert organic solvent, for example chloroform at 10 temperatures between 0 °C and the boiling point of the solvent. Compounds of formula (VI) may also be obtained by the reduction of a compound of formula (VII) :



(VII).

15 The reaction may be carried out in ethanol, in the presence of hydrogen chloride and of finely divided iron, at a temperature between 20 and 70 °C.

20 Compounds of the formula (VII) may be obtained by the reaction of a quinoline -2,3-dicarboxylic acid anhydride of formula (IV) with a 2-nitroaniline of the formula (VIII):

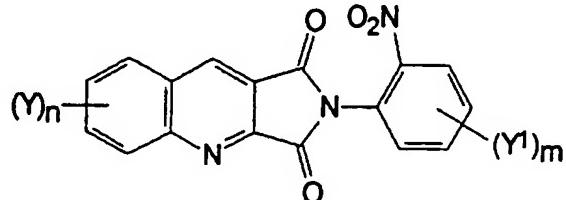


(VIII)

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in an organic solvent, for example chloroform or tetrahydrofuran, at a temperature between 20 °C and the boiling point of the solvent.

5 Compounds of formula (IIIa) may be prepared by the reduction of a compound of formula (IX):

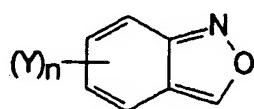


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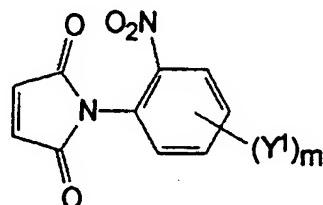
in ethanol in the presence of hydrogen chloride and of finely divided iron and at a temperature between 20 and 70 °C, or in an ethanol water mixture in the presence of sodium sulphide at a temperature between 20 °C and the boiling point of the solvent mixture.

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Compounds of formula (IX) may be prepared by the reaction of a 1,2-benzo-isoxazole of formula (X) with a maleimide of formula (XI):



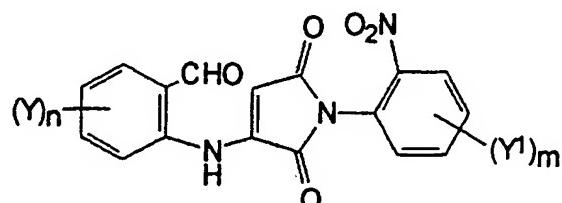
(X)



(XI)

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in a high boiling organic solvent such as xylene or o-dichlorobenzene at a temperature from 120 to 180°C. When a reaction temperature below 120°C is used the major reaction product is an aldehyde of formula (XII):



(XII)

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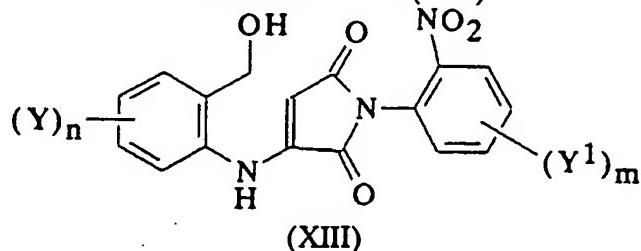
The above reaction is particularly useful for the synthesis of compounds of formula (IX) where the group Y is an electron

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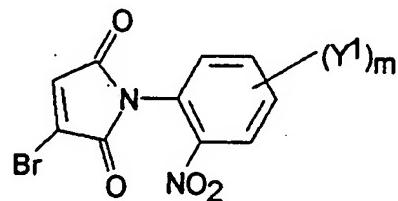
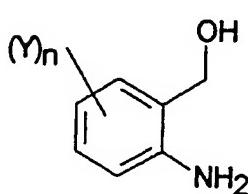
withdrawing substituent (e.g. nitro, halogen or trifluoromethyl).

5 The compound of formula (XII) may be converted into a compound of formula (IX) in the presence of a base (e.g. piperidine) in an organic solvent such as ethanol at a temperature from 20°C to the boiling point of the solvent. Alternatively the cyclisation of (XII) to (IX) can be achieved by refluxing in xylene in the presence of p-toluene sulphonic acid.

10 The intermediates of formula (XII) may also be prepared by the oxidation of an alcohol of formula (XIII):

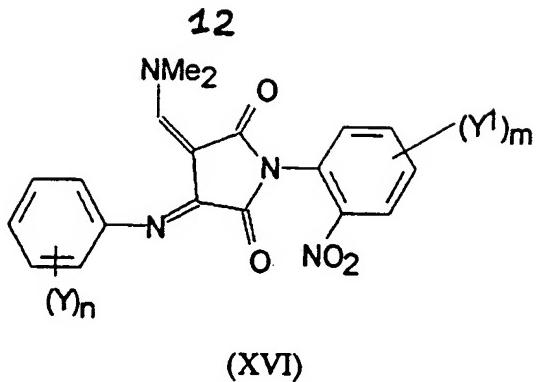


15 in the presence of an oxidising agent, for example pyridinium chlorochromate in dichloromethane at room temperature. The alcohol of formula (XIII) can be prepared by the reaction between an alcohol of formula (XIV) and a bromomaleimide of formula (XV):



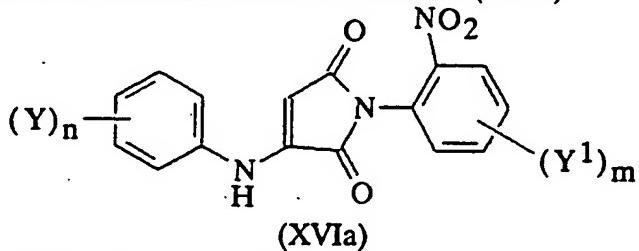
20 in an aprotic solvent such as toluene and at a temperature between 250°C and the reflux temperature of the solvent. This method is particularly useful for the synthesis of precursors to compounds of the formula (Ia) where n is one, and the group Y occupies the 5- or 7- position or, when n is 2, the groups Y which may be the same or different occupy positions 6- and 7-, or 5- and 6-, or 5- and 7- of the quinoline ring.

25 Compounds of formula (IX) may also be prepared by the method described by Maudling, J. Het. Chem. 25, 1777 (1988) which involves the cyclisation of a compound of formula (XVI):



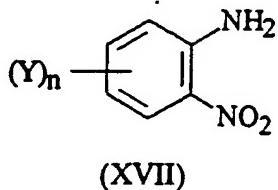
in polyphosphoric acid. This reaction is particularly useful for the synthesis of precursors to compounds of formula (Ia) in which either n is one and Y occupies the 6- or 8- position of the quinoline ring, or in which n is two and the groups Y occupy the 6- and 8- positions of the quinoline ring.

Compounds of formula (XVI) may be prepared by the reaction of an anilinomaleimide of formula (XVIa)



with dimethylformamide dimethylacetal.

The anilinomaleimides of formula (XVIa) may be prepared by the reaction of a bromomaleimide of formula (XV) and an aniline of formula (XVII) :

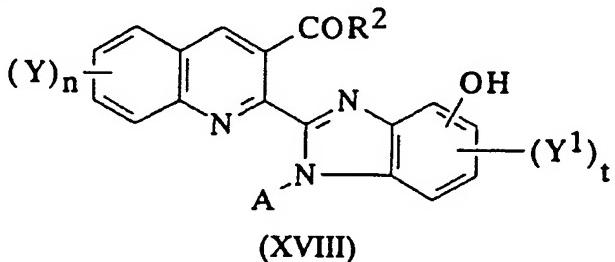


in an aprotic organic solvent such as toluene or a protic solvent, for example, ethanol and at a temperature between 25°C and the boiling point of the solvent.

According to a further feature of the invention compounds of formula (I) wherein m is 1, 2, 3 or 4 and one of the groups Y¹ represents a group -OR or -OR^{1a} which occupies the 4- or 5-position of the benzimidazole ring and in which R² represents a group -X-M wherein X is oxygen and M represents a straight or branched chain alkyl group containing up to 8 carbon atoms, or a

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cycloalkyl group containing 3-6 carbon atoms, and the group Y is as hereinbefore defined excluding the groups -NO₂, I, Cl, and Br, may be prepared by the reaction of a hydroxybenzimidazole of formula (XVIII):

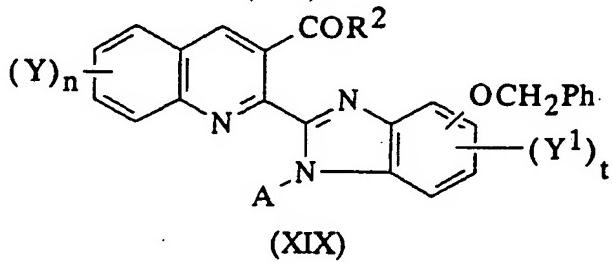


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wherein t is 0, 1, 2 or 3, with a compound (R^{1a})₋L or R-L where L represents a leaving group, for example the tosyl group or halogen (Cl, Br, I). The reaction is generally carried out in the presence of a base such as potassium carbonate in an inert organic solvent, for example acetone or DMF and at temperatures between 0°C and the reflux temperature of the solvent. Compounds of formula (XVIII) may be prepared by hydrogenolysis of a benzyloxy benzimidazole of formula (XIX):



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in a protic solvent such as methanol in the presence of hydrogen or a hydrogen donor such a 1,4-cyclohexadiene optionally in the presence of a catalytic amount of a hydrogenation catalyst for example palladium on charcoal. The reaction is generally carried out at room temperature and atmospheric pressure. Compounds of formula (XIX) can be prepared by the application of methods hereinbefore described.

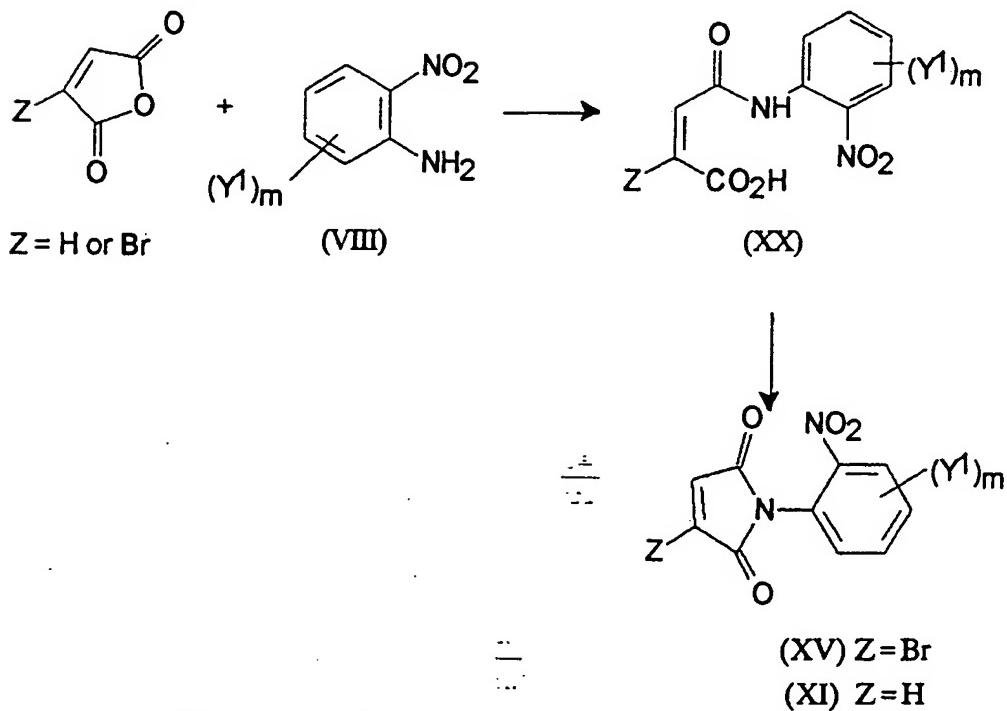
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Compounds of formula (XV) or (XI) may be prepared by the reaction of a 2-nitroaniline of formula (VIII) with bromomaleic anhydride or maleic anhydride respectively. The reaction is generally carried out in an organic solvent, for example chloroform and at a temperature between 25°C and the boiling point of the solvent to obtain an intermediate of formula (XX) which may be cyclised by heating in acetic acid at reflux temperature in the

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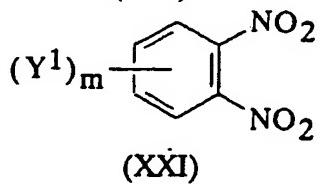
presence of sodium acetate, as illustrated in the following reaction scheme



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The 1,2-phenylenediamines of general formula (V) may be prepared by the reduction of 2-nitroanilines of formula (VIII) or of dinitrobenzenes of formula (XXI):

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(XXI)

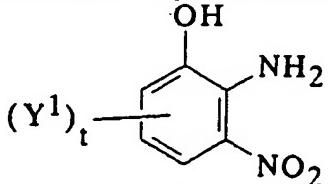
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in hydrochloric acid in the presence of stannous chloride at a temperature between 40 and 90°C, or in a mixture of a polar protic solvent, for example ethanol, and water in the presence of sodium sulphide at a temperature of between 20°C and the boiling point of the solvent mixture. Alternatively the reduction can be carried out in a polar protic solvent such as methanol in the presence of hydrogen and of a hydrogenation catalyst, for example palladium on charcoal at a temperature between 20°C and 60°C. It shall be understood that the catalytic reduction cannot be used for compounds of the formula (XXI) and (VIII) where the group $(Y^1)_m$ includes a functional group which is capable of being reduced by the said method for example $-NO_2$, halogen or when a group Y^1 contains a double or triple bond.

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Compounds of formula (VIII) wherein m is 1 or 2 and one of the groups Y¹ represents a group -OR or -OR^{1a} may be prepared by the reaction of an aminonitrophenol of formula (XXII):



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with a compound (R^{1a})-L, or R-L, wherein L is as hereinbefore defined in the presence of a base, for example potassium carbonate in an inert solvent, for example acetone or DMF and at a temperature from 0°C to the reflux temperature of

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The 2-nitroanilines of general formula (VIII), the dinitrobenzenes of formula (XXI) and the quinoline-2,3-dicarboxylic acid anhydrides of formula (IV) can be prepared by the application or adaption of known methods e.g. as described in US Patent 4,656,283. Compounds of formula (XXII) are known or can be prepared by the application and adaptation of known methods. The compounds of formula (Ia), (XVIII) and (XIX) are novel and as such constitute a feature of the invention.

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The following Examples illustrate the preparation of compounds of formula (I) and the Reference Examples illustrate the preparation of intermediates. Unless otherwise stated percentages are by weight.

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Example 1Preparation of 2-(1-N,N-dimethylsulphamoylbenzimidazol-2-yl)-6-ethylquinoline-3-carboxylic acid, compound 1.

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A solution of lithium hydroxide (0.52g) in water was added to a stirred suspension of 2-propynyl 2-(1-N,N-dimethylsulphamoylbenzimidazol-2-yl)-6-ethylquinoline-3-carboxylate (1.87g) in methanol at room temperature. The mixture was then stirred for 5 hours at 50°C. The cooled reaction mixture was filtered and evaporated under reduced pressure. The resulting yellow residue was dissolved in water, washed with ethyl acetate and then acidified with 2N hydrochloric acid to pH 1. The precipitate thus obtained was filtered and dried to give the title compound as a white solid, 1.3g, m.p. 240°C.

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By proceeding in a similar manner the following compounds of the formula I above wherein R² is -OH and A is -SO₂NMe₂ were obtained from the appropriate starting materials:

Compound No	n	Y	m	Y ¹	m.p. /°C
2	1	6-OCH ₃	0	-	279-281
3	1	6-CH ₃	0	-	245-246
4	1	8-CH ₃	0	-	182-182.5
5	2	5,8-diCH ₃	0	-	283-285
11	1	6-CH ₃	1	4-OCH ₂ C≡CH	153-155
12	1	6-CH ₃	1	4-OCH ₃	238-240
13	1	6-CH ₃	1	4-OCH ₂ CH=CH ₂	165-167
14	1	6-CH ₃	1	4-OCHF ₂	193-195
15	1	6-CH ₃	1	4-OC ₂ H ₅	186-190
16	1	6-C ₂ H ₅	1	4-OCH ₃	142-144
17	1	6-Cl	0	-	286-289
18	1	6-Cl	1	4-OCH ₃	234-238
19	1	6-Cl	1	4-OCH ₂ C≡CH	188 (dec.)

H¹ NMR.

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(a) (DMSO-d₆) d = 2.60 (3H,s), 2.87 (6H,s), 3.75 (3H,s), 4.80 (2H,d), 5.80 (1H,dd),
 5.84 (1H,dd), 6.10 (1H,M), 7.00 (1H,d), 7.40 (1H,t), 7.50 (1H,d), 7.88 (1H,d),
 8.05 (1H,d), 8.10 (1H,s), 9.07 (1H,s) ppm.

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(b) (DMSO-d₆) d = 2.60 (3H,s), 2.90 (6H,s), 3.30 (1H,s), 3.75 (3H,s), 7.38 (1H,d),
 7.55 (1H,t), 7.80 (1H,t), 7.90 (1H,d), 8.05 (1H, d), 8.10 (1H, br s), 9.10 (1H,s) ppm.

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Example 2
Preparation of 2-propynyl 2-(1-N,N-dimethylsulphamoyl-benzimidazol-2-yl)-6-ethyl-quinoline-3-carboxylate, compound 6.

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A mixture of anhydrous potassium carbonate (7.4g) and 2-propynyl 2-(1H-benzimidazol-2-yl)-6-ethylquinoline-3-carboxylate (6.4g) in anhydrous acetonitrile was stirred at reflux for 4 hours. To the cooled reaction mixture was added dimethylsulphamoyl chloride (7.7g) and then the mixture was heated at reflux for 12 hours. The solvent was then evaporated and the residue suspended in water and extracted with dichloromethane. The organic phase was dried

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over magnesium sulphate, filtered and evaporated. The residue was crystallised from ethyl acetate to give the title compound as a white solid, 2.2 g, m.p. 194°C.

5 By proceeding in a similar manner the following compounds of formula I above wherein A is $-\text{SO}_2\text{NMe}_2$ were obtained from the appropriate starting materials:

Cmpd. No.	n	Y	m	Y ¹	R ²	m.p. /°C
7	1	6-OCH ₃	0	-	4-OCH ₂ C≡CH	187-189
8	1	6-CH ₃	0	-	OCH ₃	200-201
9	1	8-CH ₃	0	-	4-OCH ₂ C≡CH	203-205
10	2	5,8-diCH ₃	0	-	4-OCH ₂ C≡CH	200-201
20	1	6-CH ₃	1	4-OCH ₂ C≡CH	OCH ₃	183-185
21	1	6-CH ₃	1	4-OCH ₃	OCH ₃	198-200
22	1	6-CH ₃	1	4-OCH ₂ CH=CH ₂	OCH ₃	nmr (a)
23	1	6-CH ₃	1	4-OCHF ₂	OCH ₃	nmr (b)
24	1	6-CH ₃	1	4-OC ₂ H ₅	OCH ₃	197-199
25	1	6-C ₂ H ₅	1	4-OCH ₃	OCH ₃	178-180
26	1	6-Cl	0	-	OCH ₃	219-220
27	1	6-Cl	1	4-OCH ₃	OCH ₃	193-195
28	1	6-Cl	1	4-OCH ₂ C≡CH	OCH ₃	184-186

Reference Example 1

4-Ethylquinolo[2',3':3,4]pyrrolo[1,2-a]benzimidazol-7-one

A mixture of 6-ethylquinoline-2,3-dicarboxylic acid anhydride

10 (8.9g) (prepared as in US Patent 4,656,283) and o-phenylenediamine (4.2g) in acetic acid (77 ml) was heated at reflux temperature for 6 hours. To the cooled solution was added acetic anhydride (17 ml) and the resulting mixture heated at reflux for 4 hours to give after cooling a brown precipitate which was filtered and washed with diethyl ether and dried to give the title compound as a yellow solid, 5.82 g, m.p. 254°C.

15 By proceeding in a similar manner the following compounds of formula (II) above were obtained from the appropriate starting materials

n	Y	m	Y ¹	m.p. /°C
1	4-OCH ₃	0	-	302-303
1	4-CH ₃	0	-	279
1	2-CH ₃	0	-	239-240
2	2,5-CH ₃	0	-	232-233
1	4-CH ₃	1	9-OCH ₂ C≡CH	241-245
1	4-CH ₃	1	9-OCH ₃	323.5-325
1	4-CH ₃	1	9-OCH ₂ CH=CH ₂	212-215
1	4-CH ₃	1	9-OCHF ₂	252-255
1	4-CH ₃	1	9-OC ₂ H ₅	238-241
1	4-C ₂ H ₅	1	9-OCH ₃	245-246
1	4-Cl	0	-	311-313
1	4-Cl	1	9-OCH ₃	320-322
1	4-Cl	1	9-OCH ₂ C≡CH	>340

Reference Example 2Preparation of 2-propynyl 2-(2H-benzimidazol-2-yl)-6-ethylquinoline-3-carboxylate.

5 Triethylamine (3 ml) was added to a stirred solution of 4-ethylquinolo[2',3':3,4] pyrrolo[1,2-a]benzimidazol-7-one (5.8g) and propargyl alcohol (2.2g) in dichloromethane at room temperature. The mixture was stirred for 14 hours then the resulting yellow solution was washed three times with water. The combined
 10 aqueous washings were extracted with dichloromethane and then the combined organic extracts were dried over magnesium sulphate and evaporated to give the title compound as a white solid, 6.4g, m.p. 167°C.

15 By proceeding in a similar manner the following compounds of the formula (Ia) above were obtained from the appropriate quinolo[2',3':3,4]pyrrolo [1,2-a]benzimidazol-5-one and alcohol:

n	Y	m	Y ¹	R ²	m.p./°C
1	6-OCH ₃	0	-	OCH ₂ C≡CH	189-191
1	6-CH ₃	0	-	OCH ₃	182
1	8-CH ₃	0	-	OCH ₂ C≡CH	213-215
2	5,8-diCH ₃	0	-	OCH ₂ C≡CH	222-233
1	6-CH ₃	1	4-OCH ₂ C≡CH	OCH ₃	172-175
1	6-CH ₃	1	4-OCH ₃	OCH ₃	82-84

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1	6-CH ₃	1	4-OCH ₂ CH=CH ₂	OCH ₃	nmr (c)
1	6-CH ₃	1	4-OCHF ₂	OCH ₃	177-180
1	6-CH ₃	1	4-OC ₂ H ₅	OCH ₃	nmr (d)
1	6-C ₂ H ₅	1	4-OCH ₃	OCH ₃	nmr (e)
1	6-Cl	0	-	OCH ₃	nmr (f)
1	6-Cl	1	4-OCH ₃	OCH ₃	nmr (g)
1	6-Cl	1	4-OCH ₂ C≡CH	OCH ₃	nmr (h)

¹H NMR.

(c) (DMSO-d₆) d = 2.55 (3H,S), 4.10 (3H,s), 4.80 (2H,d), 5.38 (1H,d), 6.28 (1H,m), 6.75 (1H,d), 7.20 (1H,d), 7.30 (1H,d), 7.60 (2H,m), 8.05 (1H, d), 8.25 (1H, d) ppm.

5 (d) (CDCl₃) d = 1.55 (3H, t), 2.60 (3H,s), 4.10 (3H,s), 4.30 (2H,q), 6.75 (1H,d), 7.20 (1H,t), 7.30 (1H,d), 7.65 (2H,m), 8.05 (1H,d), 8.30 (1H,s) ppm.

10 (e) (DMSO-d₆) d = 1.30 (3H,t), 2.87 (2H,q), 3.9 (3H,s), 4.00 (3H,s), 6.75 (1H,m), 7.20 (2H,m), 7.85 (1H,dd), 7.95 (1H, m), 8.10 (1H,d), 8.60 (1H,s), 13.2 (1H,s) ppm.

(f) (DMSO-d₆)d = 3.90 (3H,s), 7.25 (2H,m), 7.97 (1H,d), 8.20 (1H,d), 8.30 (1H,s), 8.70 (1H,s), 13.3 (1H,br s) ppm.

(g) (DMSO-d₆) d = 3.35 (3H,s), 4.00 (3H,s), 6.75 (1H,d), 7.70 (2H,m), 7.95 (1H,d), 8.20 (1H,d), 8.70 (1H,d), 8.80 (1H,d), 13.20 (1H,br s) ppm.

15 (h) (DMSO-d₆) d = 3.60 (1H,t), 3.95 (3H,t), 5.15 (2H,d), 6.85 (1H, dd), 7.25 (2H,m), 7.97 (1H, dd), 8.20 (1H,d), 8.30 (1H,s), 8.70 (1H,s), 13.38 (1H,s) ppm.

Reference Example 3Preparation of 3-(difluoromethoxy)-1,2-benzenediamine.

20 A mixture of 6-difluoromethoxy-2-nitroaniline (28.8g) and sodium sulphide anhydrate (152g) in a mixture of ethanol and water was heated at reflux with stirring for 12 hours. The resulting brown solution was cooled and then concentrated in vacuo. The residue was dissolved in dichloromethane and washed with brine. The organic phase was dried over magnesium sulphate and then evaporated to give the title compound as a solid(22 g), ¹H NMR (DMSO-D₆) d = 4.32 (2H,br s), 4.75 (2H,br s), 6.40 (3H,m), 6.98 (1H,t) ppm.

Reference Example 4Preparation of 6-difluoromethoxy-2-nitroaniline.

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A solution of sodium hydroxide (2M, 1.6L) was added to a stirred solution of 2-amino-3-nitrophenol (100g) in dioxan. Chlorodifluoromethane was then bubbled into the reaction mixture for two hours. The solution was extracted with dichloromethane and the combined organic extracts washed with 2M sodium hydroxide solution and then brine. After drying over magnesium sulphate the solvent was evaporated to give the title compound as a brown solid (77.2g), m.p. 47-49°C.

Industrial Applicability

According to a feature of the present invention, there is provided a method for controlling the growth of weeds (i.e. undesired vegetation) at a locus which comprises applying to the locus a herbicidally effective amount of at least one benzimidazolyl quinoline-3-carboxylate derivative of general formula (I) or an agriculturally acceptable salt thereof. For this purpose, the benzimidazolyl quinoline-3-carboxylate derivatives are normally used in the form of herbicidal compositions (i.e. in association with compatible diluents or carriers and/or surface active agents suitable for use in herbicidal compositions), for example as hereinafter described.

The compounds of general formula (I) show herbicidal activity against dicotyledonous (i.e. broad-leaved) and monocotyledonous (e.g. grass) weeds by pre- and/or post-emergence application.

The amounts of compounds of general formula (I) applied vary with the nature of the weeds, the compositions used, the time of application, the climatic and edaphic conditions and (when used to control the growth of weeds in crop-growing areas) the nature of the crops. When applied to a crop-growing area, the rate of application should be sufficient to control the growth of weeds without causing substantial permanent damage to the crop. In general, taking these factors into account, application rates between 0.01kg and 5kg of active material per hectare give good results. However, it is to be understood that higher or lower application rates may be used, depending upon the particular problem of weed control encountered.

Representative compounds of general formula (I) have been used in herbicidal applications according to the following procedures.

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	<u>Weed species</u>	<u>Approx number of seeds/pot</u>
5	1) <u>Broad-leaved weeds</u>	
	Abutilon theophrasti	10
	Amaranthus retroflexus	20
	Galium aparine	10
	Ipomoea purpurea	10
	Sinapis arvensis	15
	Xanthium strumarium	2.
10	2) <u>Grass weeds</u>	
	Alopecurus myosuroides	15
	Avena fatua	10
	Echinochloa crus-galli	15
	Setaria viridis	20.
15	3) <u>Sedges</u>	
	Cyperus esculentus	3.
	<u>Crop</u>	
20	1) <u>Broad-leaved</u>	
	Cotton	3
	Soya	3.
	2) <u>Grass</u>	
	Maize	2
	Rice	6
	Wheat	6.
25		

The compounds of the invention were applied to the soil surface, containing the seeds, as described in (a). A single pot of each crop and each weed was allocated to each treatment, with unsprayed controls and controls sprayed with acetone alone.

30 After treatment the pots were placed on capillary matting kept in a glass house, and watered overhead. Visual assessment of crop damage was made 20-24 days after spraying. The results were expressed as the percentage reduction in growth or damage to the crop or weeds, in comparison with the plants in the control pots.

35 c) Weed control : Post-emergence

The weeds and crops were sown directly into John Innes potting compost in 75 mm deep, 70 mm square pots except for Amaranthus which was pricked out at the seedling stage and

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transferred to the pots one week before spraying. The plants were then grown in the greenhouse until ready for spraying with the compounds used to treat the plants. The number of plants per pot were as follows :-

5 1) Broad leafed weeds

	<u>Weed species</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
	Abutilon theophrasti	3	1-2 leaves
	Amaranthus retroflexus	4	1-2 leaves
	Galium aparine	3	1 st whorl
10	Ipomoea purpurea	3	1-2 leaves
	Sinapis arvensis	4	2 leaves
	Xanthium strumarium	1	2-3 leaves.

2) Grass weeds

	<u>Weed species</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
15	Alopecurus myosuroides	8-12	1-2 leaves
	Avena fatua	12-18	1-2 leaves
	Echinochloa crus-galli	4	2-3 leaves
	Setaria viridis	15-25	1-2 leaves.

3) Sedges

	<u>Weed species</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
20	Cyperus esculentus	3	3 leaves.

1) Broad leafed

	<u>Crops</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
25	Cotton	2	1 leaf
	Soya	2	2 leaves.

2) Grass

	<u>Crops</u>	<u>Number of plants per pot</u>	<u>Growth stage</u>
30	Maize	2	2-3 leaves
	Rice	4	2-3 leaves
	Wheat	5	2-3 leaves.

The compounds used to treat the plants were applied to the plants as described in (a). A single pot of each crop and weed species was allocated to each treatment, with unsprayed controls and controls sprayed with acetone alone.

35 After treatment the pots were placed on capillary matting in a glass house, and watered overhead once after 24 hours and then by controlled sub-irrigation. Visual assessment of crop damage and weed control was made 20-24 days after spraying. The results were

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expressed as the percentage reduction in growth or damage to the crop or weeds, in comparison with the plants in the control pots.

Representative compounds of the invention used at 4000 g/ha or less, have shown an excellent level of herbicidal activity in the foregoing experiments, giving 90% reduction in growth of one or more weed species when applied pre- or post- emergence, combined with tolerance on one or more crops.

When applied pre-emergence at 1000 g/ha or less, compounds 1, 3, 11, 12, 13, 14, 15, 16, 17, 18 and 19 gave 90% reduction in growth of one or more weed species with tolerance on one or more crop species. When applied post-emergence at 1000 g/ha or less, compounds 1, 2, 3, 6, 7, 11, 12, 13, 14, 15, 16, 17, 18 and 19 gave 90% reduction in growth of one or more weed species with tolerance on one or more crop species.

According to a further feature of the present invention, there are provided herbicidal compositions comprising one or more of the benzimidazolyl quinoline-3-carboxylate derivatives of formula I or an agriculturally acceptable salt thereof, in association with, and preferably homogeneously dispersed in, one or more compatible agriculturally- acceptable diluents or carriers and/or surface active agents [i.e. diluents or carriers and/or surface active agents of the type generally accepted in the art as being suitable for use in herbicidal compositions and which are compatible with compounds of general formula (I)]. The term "herbicidal compositions" is used in a broad sense to include not only compositions which are ready for use as herbicides but also concentrates which must be diluted before use. The herbicidal compositions may contain both a diluent or carrier and surface-active (e.g. wetting, dispersing, or emulsifying) agent.

Herbicidal compositions according to the present invention may also comprise the compounds of general formula (I) in association with, and preferably homogeneously dispersed in, one or more other pesticidally active compounds and, if desired, one or more compatible pesticidally acceptable diluents or carriers, surface-active agents and conventional adjuvants as hereinbefore described.

Pesticidally active compounds and other biologically active materials which may be included in, or used in conjunction with, the

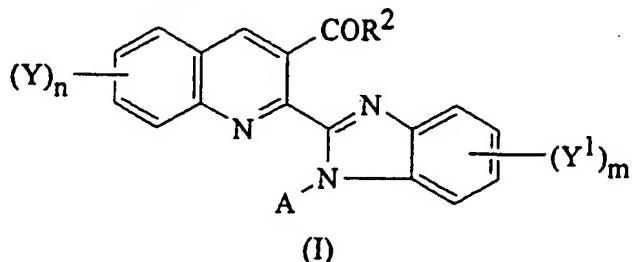
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herbicidal compositions of the present invention, for example those hereinbefore mentioned, and which are acids, may, if desired, be utilized in the form of conventional derivatives, for example alkali metal and amine salts and esters.

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CLAIMS

1. A benzimidazolyl quinoline-3-carboxylate derivative of formula I :-



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wherein Y represents:

10 a straight- or branched- chain alkyl group containing up to eight carbon atoms which is optionally substituted by one or more R¹ groups which may be the same or different; or

15 a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or

20 a group selected from -SR, -S(O)R, -SO₂R, -OR, halogen, nitro, cyano, -NR⁷R⁸, aryl or O-aryl;

25 Y¹ represents:-

a straight- or branched- chain alkyl, alkenyl or alkynyl group containing up to eight carbon atoms which is optionally substituted by one or more R¹ groups which may be the same or different; or

30 a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or

a group selected from -SR, -OR, -OR^{1a}, halogen, aryl, aralkyl, O-aryl, -NR⁷R⁸ or -OCH₂R¹¹;

R² represents:-

35 a group -OH -NR⁷R⁸ or -X-M, where X represents oxygen or sulphur, and

M represents:-

40 a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more R¹ groups which may be the same or different;

45 a cycloalkyl group containing from three to six carbon atoms optionally substituted by one or more R¹ groups which may be the same or different; or

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a group selected from aryl, aralkyl, $-(CR^{41}R^{42})_q-C\equiv CR^6$, $-(CR^{41}R^{42})_q-C(R^4)=CR^5R^6$ and $-N=CR^9R^{10}$;

A represents $-SO_2NR^7R^8$;

R represents:-

5 a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more groups R¹ which may be the same or different;

10 or a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more groups R³ which may be the same or different;

R¹ represents:-

15 a group selected from -OR³, -S(O)_sR³, wherein s is zero, one or two, halogen, a cycloalkyl group containing from 3 to 6 carbon atoms (optionally substituted by one or more groups R¹ which may be the same or different, other than cycloalkyl), R³, O-aryl, cyano or -CO₂R⁵;

R^{1a} is $-(CR^{41}R^{42})_r-C\equiv CR^6$ or $-(CR^{41}R^{42})_r-C(R^4)=CR^5R^6$;

20 R³ represents a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more halogen atoms which may be the same or different;

R⁴, R⁴¹, R⁴² and R⁵, which may be the same or different, each represent hydrogen or a straight- or branched- chain alkyl group containing up to 6 carbon atoms optionally substituted by one or more halogen atoms which may be the same or different; or aryl;

25 R⁶ represents a group selected from R⁴ or aralkyl;

R⁷ and R⁸, which may be the same or different, each represent:-

a hydrogen atom, or

30 a group selected from R, -OR³, -S(O)_sR³, halogen, R³, O-aryl, aryl or aralkyl; or R⁷ and R⁸ may form together with the nitrogen to which they are attached a heterocycle containing from 3 to 6 carbon atoms in the ring and zero, 1 or 2 additional heteroatoms in the ring selected from nitrogen, oxygen and sulphur;

35 R⁹ and R¹⁰, which may be the same or different, each represent:

a hydrogen atom, or

a straight- or branched- chain alkyl group containing up to eight carbon atoms optionally substituted by one or more groups,

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- which may be the same or different, selected from halogen,-OR or -S(O)_sR, where s is zero, 1 or 2; or
- 5 a phenyl group optionally substituted by from one to four groups, which may be the same or different, selected from nitro, R, -NR⁴R⁵, halogen or -S(O)_sR; or
- a 5 or 6 membered heterocycle containing from 3 to 5 carbon atoms in the ring and one or more heteroatoms in the ring selected from nitrogen, sulphur or oxygen, optionally substituted by one or more groups R¹ which may be the same or different;
- 10 or R⁹ and R¹⁰ may form together with the nitrogen to which they are attached a heterocycle containing 4 or 5 carbon atoms in the ring, which may be optionally substituted by from 1 to 3 groups R³ which may be the same or different;
- 15 R¹¹ represents a five or six membered aliphatic ring comprising an oxygen atom in the ring;
- 'aryl' represents:-
- 20 a phenyl group optionally substituted by from one to four groups which may be the same or different selected from -OR³, -SR³, halogen or R³;
- or a 5 or 6 membered heterocycle containing from 3 to 5 carbon atoms in the ring and one or more heteroatoms in the ring selected from nitrogen, sulphur or oxygen, optionally substituted by one or more groups, which may be the same or different, selected from -OR³, -SR³, halogen or R³;
- 25 aralkyl represents a group-(CR⁴R⁵)_p-aryl;
- m represents zero or an integer from 1 to 4, the groups Y¹ being the same or different when m is greater than 1;
- n represents an integer from 1 to 4; p represents one or two;
- q represents one or two; r represents an integer from 1 to 5;
- 30 where p, q or r is greater than 1, the groups -(CR⁴R⁵)- and the groups -(CR⁴¹R⁴²)- may be the same or different;
- where n is greater than 1 no more than one of the groups Y represents nitro, -SR, -SOR, -SO₂R, nitro, -NR⁷R⁸, aryl or O-aryl;
- 35 or an agriculturally acceptable salt thereof.
2. A compound according to claim 1 wherein:
- (a) A represents a group -SO₂NR⁷R⁸ in which R⁷ and R⁸ each represents an alkyl group; and/or

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- (b) R² represents a group -OH, -XM or -XW in which X is oxygen, M is alkynyl and W is an agriculturally acceptable cation; and/or
- 5 (c) Y represents alkyl, and n is 1 or 2; and/or
- (d) Y¹ represents -OR, SR, -OR^{1a} or -SR^{1a}; and m is 0, 1 or 2.

10 3. A compound according to claim 1 wherein the benzimidazole ring is substituted in the 4- and/or 5- position by a group Y¹.

15 4. A compound according to claim 1 wherein the benzimidazole ring is substituted in the 4- position and Y¹ is a group selected from methyl, methoxy, ethoxy, n-propyloxy, allyloxy, propargyloxy, 2-methoxyethoxy and chlorine.

20 5. A compound according to claim 1 wherein Y represents methyl, ethyl or chlorine.

6. A compound according to claim 1 wherein n is one and the group Y is in the 6- position of the quinoline ring.

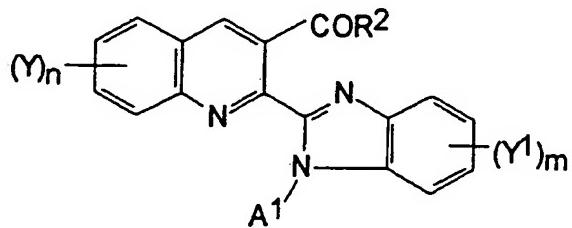
25 7. A compound according to claim 1 wherein m is one and the group Y¹ is in the 4- or 5- position of the benzimidazole ring.

30 8. A herbicidal composition which comprises as active ingredient a herbicidally effective amount of a benzimidazolyl quinoline-3-carboxylate derivative of formula I as defined in claim 1 or an agriculturally acceptable salt thereof, in association with an agriculturally acceptable diluent or carrier and/or surface active agent.

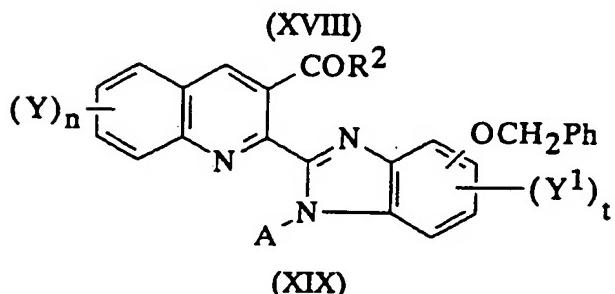
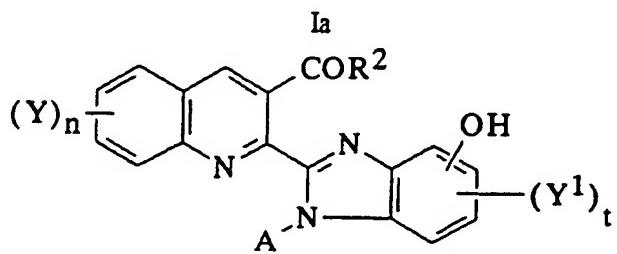
35 9. A method for controlling the growth of weeds at a locus which comprises applying to the locus a herbicidally effective amount of a benzimidazolyl quinoline-3-carboxylate derivative of formula I as defined in claim 1 or an agriculturally acceptable salt thereof.

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10. A compound useful as an intermediate in the synthesis of herbicidal compounds, characterised by the formula Ia, XIII or XIX:



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in which Y, Y¹, R², A, n and m are as defined in claim 1, A¹ is the hydrogen atom, t is 0, 1, 2 or 3 and R² is -XM or -NR⁷R⁸, wherein X, M, R⁷ and R⁸ are as defined in claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 94/00035

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07D401/04 A01N43/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 429 372 (RHONE-POULENC AGROCHEMIE) 29 May 1991 cited in the application *see whole document, especially examples pages 16-21* ---	1-10
Y	EP,A,0 509 717 (RHONE POULENC AGRICULTURE LTD.) 21 October 1992 *see whole document, especially definition of Y when n=2 or 3 , examples 5,9,12, and compounds of formulae XIV and XV*	1-10
Y	EP,A,0 508 800 (RHONE POULENC AGRICULTURE LTD) 14 October 1992 *see definition of Y, especially when n=2, and examples on pages 24-26, and compounds of formulae Ia and XIV*	1-10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
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- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

Date of mailing of the international search report

7 March 1994

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern'l Application No

PCT/EP 94/00035

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